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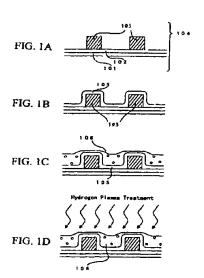
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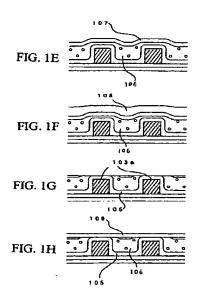
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(54)Method and apparatus for forming an interlayer insulating film, and semiconductor device

(57)Disclosed is a method for forming an interlayer insulating film which comprises the steps of forming an underlying insulating film (105) on a substrate (104); forming a porous SiO2 film (106) on the underlying insulating film (105) by chemical vapor deposition method using Si₂H₆ and an oxidative gas as a reaction gas; subjecting the porous SiO₂ film (106) to H (hydrogen) plasma treatment; forming a plasma SiO₂ film (107) and a fluidic SiO2 film (108) formed by TEOS+O3 on the porous SiO₂ film (106); then smoothing a surface of the SiO₂ film by etching; and forming a cover insulating film (109) on the smoothed surface.





Description

BACKGROUND OF THE INVENTION

[0001] The present invention relates to a method for forming an interlayer insulating film and, more particularly, to a method for forming an interlayer insulating film having a low dielectric constant, which is necessary for a highly-integlated semiconductor device. A progress in high integlation regarding the semiconductor device in recent years has resulted in a narrower interval between wiring lines. As the narrowed interval between the wiring lines causes an increase in capacitance between the wiring lines, a request has been made for formation of an interlayer insulating film, which has a low dielectric constant.

[0002] With recent progresses in high integration of an LSI device, the wiring line has been micronized and multi-layered. There has also been an increase in capacitance between the wiring lines. Such an increase in capacitance has caused a great reduction in an operating speed. Thus, improvement in this regard has been strongly demanded. As one of improvement measures, a method for reducing capacitance between the wiring lines has been studied. This method uses an interlayer insulating film, which has a dielectric constant lower than that of SiO₂ currently used for an interlayer insulating film.

[0003] Typical interlayer insulating films of low dielectric constants currently under study are ① an SiOF film, and ② an organic insulating film of a low dielectric constant. Description will now be made of these films.

1 SiOF Film

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[0004] An SiOF film is formed by using source gas containing F and substituting Si-F bond for a portion of Si-O bond in SiO₂. This SiOF film has a relative dielectric constant, which is monotonically reduced as concentration of F in the film increases.

[0005] For forming such SiOF films, several methods have been reported (see p.82 of monthly periodical "Semiconductor World", February issue of 1996). Most promising among these methods is one for forming an SiOF film by using SiH_4 , O_2 , Ar and SiF_4 as source gases, and by a high-density plasma enhanced CVD method (HDPCVD method). A relative dielectric constant of an SiOF film formed by this method is in a range of 3.1 to 4.0 (varies depending on F concentration in the film). This value is lower than a relative dielectric constant 4.0 of SiO_2 , which has conventionally been used for the interlayer insulating film.

② Organic Insulating Film of Low Dielectric Constant

[0006] As an insulating film which has a lower dielectric constant (3.0 or lower) compared with the SiOF film, an organic insulating film of a low dielectric constant is now a focus of attention. Table 1 shows a few organic insulating films of low dielectric constants, which have been reported, and respective relative dielectric constants and thermal decomposition temperatures thereof.

TABLE 1

Organic Insulating Film	Relative Dielectric Con- stant	Thermal Decomposition Temperature (°C)	Note
Fluorine-containing resin	2.4	420	p.82 of monthly periodical "Sem- iconductor World", February issue of 1997
Cytop	2.1	400	p. 90 of monthly periodical "Sem- iconductor World", February issue of 1996
Amorphous telon	1.9	400	p. 91 of monthly periodical "Sem- iconductor World", February issue of 1996

[0007] However, the SiOF film is disadvantageous in that an increase in concentration of F in the film leads to a reduction in moisture absorption resistance. The reduced moisture absorption resistance poses a serious problem, because a transistor characteristic and adhesion of an upper barrier metal layer are affected.

[0008] Peeling-off easily occurs in the organic insulating film of a low dielectric constant, because of bad adhesion

with a silicon wafer or the SiO₂ film. Furthermore, the organic insulating film is disadvantageous in that heat resistivity is low since a thermal decomposition temperature is around 400 °C. The disadvantage of low heat resistivity poses a problem for annealing a wafer at a high temperature.

SUMMARY OF THE INVENTION

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[0009] It is an object of the present invention to provide a method for forming an interlayer insulating film having good moisture absorption resistance and heat resistivity and a low dielectric constant, a semiconductor device using the interlayer insulating film, and a semiconductor manufacturing apparatus for forming the interlayer insulating film.

[0010] According to the method for forming the interlayer insulating film according to the present invention, an underlying insulating film is formed on an object to be formed (a substrate), and then a porous SiO₂ film is formed on the underlying insulating film. This porous SiO₂ film is formed by three following methods.

- (1) Chemical vapor deposition method using Si_2H_6 and O_2 or Si_3H_8 and O_2 as a reaction gas as illustrated in Fig. 1C
- [0011] The present inventor found that this method is used whereby Si_2H_6 and O_2 or Si_3H_8 and O_2 react with each other in a vapor phase and particulate SiO_2 is formed in the vapor phase. Particulate SiO_2 is deposited on an underlying insulating film 105. The surface of underlying insulating film 105 can not be densely filled with particulate SiO_2 due to a shape of particulate SiO_2 . Thus, an SiO_2 film 106 having many voids is formed on the underlying insulating film 105.
- (2) Method in which plasma is intermittently or periodically generated in an atmosphere of SiH_4 and O_2 under a low pressure as illustrated in Figs. 3C and 4
- [0012] The present inventor found that the plasma is generated in the atmosphere of SiH_4 and O_2 under the low pressure whereby particulate SiO_2 is formed in the vapor phase. The surface of the substrate can not be densely filled with particulate SiO_2 due to the shape of particulate SiO_2 . Thus, the particulate SiO_2 is deposited on the substrate, so that the porous SiO_2 film is formed on the substrate.
- [0013] The present inventor further found that the porous SiO_2 film and a SiO_2 film formed by typical low pressure chemical vapor deposition are laminated whereby the porous SiO_2 film having a stable film quality is formed. The inventor invented the method in which the plasma is intermittently or periodically generated in the atmosphere of SiH_4 and O_2 under the low pressure, as the method for laminating these films. Fig. 4 shows an example of the plasma which is periodically generated. In this drawing, plasma enhanced chemical vapor deposition method is performed under the low pressure during a time period from T1 to T2. The low pressure chemical vapor deposition method is performed during the time period from T2 to T3.
- (3) Method in which an organic film and the SiO_2 film are alternately laminated and then the film is subjected to O (oxygen) plasma treatment as illustrated in Figs. 6C and 6D
- [0014] According to this method, a film 506 having the organic film and the SiO₂ film, these films being alternately laminated, is first formed. Then, the film 506 is subjected to the O (oxygen) plasma treatment. The O (oxygen) plasma treatment is thus performed, whereby the organic film previously formed is selectively removed and thus the voids are created in an area in the film in which the organic film is formed. Thus, SiO₂ alone remains in the film and many voids are created. That is, a porous SiO₂ film 507 is formed.
- (4) H (hydrogen) plasma treatment for the porous SiO₂ film
 - [0015] The porous SiO_2 film formed as described above has many voids in the film. Thus, a surface area of the porous SiO_2 film is larger than the surface area of the SiO_2 film having no void. Thus, the porous SiO_2 film is prone to adsorb moisture in the air. As illustrated in Figs. 1D, 3D and 6E, the porous SiO_2 film is subjected to the H (hydrogen) plasma treatment. Thus, a dangling bond in an Si-O bond on the inner surface of the voids is replaced by an Si-H bond. Consequently, it is possible to prevent the moisture from being adsorbed on the inner surface of the voids.
 - (5) Formation of a cover insulating film
- [0016] As illustrated in Fig. 1E, the porous SiO₂ film is subjected to the H (hydrogen) plasma treatment, and then the porous SiO₂ film is covered with a cover insulating film 109. Thus, it is possible to further prevent the moisture from being adsorbed on the surface of the porous SiO₂ film 106.
 - [0017] Moreover, as illustrated in Fig. 8, the semiconductor manufacturing apparatus according to the present

invention has control means for controlling flow rate control means for controlling a flow rate of the reaction gas and switching means for switching a high-frequency power applied to a chamber.

[0018] As illustrated in Fig. 4, this control means can alternately repeat the plasma enhanced chemical vapor deposition under the low pressure and the low pressure chemical vapor deposition in one chamber under the low pressure. That is, in Fig. 10, during the time period from T1 to T2, the reaction gases (SiH₄, O₂ and Ar) are introduced into the chamber and the high-frequency power is applied to the chamber, so that the plasma enhanced chemical vapor deposition under the low pressure is performed. During the time period from T2 to T3, the reaction gases (SiH₄, O₂ and Ar) are introduced into the chamber which the high-frequency power is not applied to, so that the low pressure chemical vapor deposition is performed.

[0019] Furthermore, as illustrated in Fig. 7, this control means can alternately repeat a process for forming the organic film by using the plasma enhanced chemical vapor deposition method and a process for forming the SiO₂ film by using the plasma enhanced chemical vapor deposition method in one chamber which the high-frequency power is applied to. That is, in Fig. 7, during the time period from T1 to T2, the reaction gas (a CH compound) for forming the organic film is introduced into the chamber which the high-frequency power is applied to, so that the organic film is formed. During the time period from T2 to T3, the reaction gases (SiH₄ and O₂) for forming the SiO₂ film are introduced into the chamber which the high-frequency power is applied to, so that the SiO₂ film is formed.

BRIEF DESCRIPTION OF THE DRAWINGS

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Figs. 1A to 1H are cross - sectional views showing a method for forming an interlayer insulating film according to a first embodiment of the present invention;

Figs. 2A to 2M are cross - sectional views showing the method for forming the interlayer insulating film according to a second embodiment of the present invention;

Figs. 3A to 3I are cross - sectional views showing the method for forming the interlayer insulating film according to a third embodiment of the present invention;

Fig. 4 shows characteristics of time dependency of an SiH4 flow rate, an O_2 flow rate, an Ar flow rate and an RF power applied to a chamber in the method for forming the interlayer insulating film according to the third and fourth embodiments of the present invention and a semiconductor manufacturing apparatus according to a sixth embodiment of the present invention;

Figs. 5A to 5M are cross - sectional views showing the method for forming the interlayer insulating film according to the fourth embodiment of the present invention;

Figs. 6A to 6J are cross - sectional views showing the method for forming the interlayer insulating film according to a fifth embodiment of the present invention;

Fig. 7 shows the characteristics of the time dependency of the flow rate of a reaction gas (a CH compound) for forming an organic film and the flow rate of a reaction gas ($SiH_4 + O_2$) for forming an SiO_2 film in the method for forming the interlayer insulating film according to the fifth embodiment of the present invention and the semiconductor manufacturing apparatus according to the sixth embodiment of the present invention; and

Fig. 8 shows a constitution of the semiconductor manufacturing apparatus according to the sixth embodiment of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

- 45 [0021] Next, embodiments of the present invention will be described with reference to the accompanying drawings.
 - (1) Description of methods for forming an interlayer insulating film according to the embodiments of the present invention
- (a) First embodiment

[0022] Figs. 1A to 1H are cross sectional views for describing the first embodiment.

[0023] First, as shown in Fig. 1A, a BPSG (borophosphosilicate glass) film 102 is formed on a silicon substrate 101. Then, an aluminum film is formed on the BPSG film 102 and then the aluminum film is patterned, whereby an aluminum wiring layer 103 is formed. A substrate 104 comprises the silicon substrate 101, the BPSG film 102 and the aluminum wiring layer 103.

[0024] Next, as shown in Fig. 1B, an SiO₂ film 105 (an underlying insulating film) is formed on the substrate 104. This SiO₂ film 105 is formed by a plasma enhanced CVD method (plasma enhanced Chemical Vapor Deposition

method). SiH₄ and N₂O are used as a reaction gas. A thickness of the SiO₂ film 105 is 100 nm.

[0025] Subsequently, as shown in Fig. 1C, an SiO_2 film 106 is formed on the SiO_2 film 105. This SiO_2 film 106 is formed by CVD (Chemical Vapor Deposition) using Si_2H_6 and O_3 as the reaction gas. When these reaction gases are used, SiO_2 having large particles is formed in a vapor phase and SiO_2 having large particles is deposited on the SiO_2 film 105. Thus, the SiO_2 film 106 has many voids in the film. Consequently, the SiO_2 film 106 is a porous SiO_2 film. The thickness of the porous SiO_2 film 106 is 500 nm.

[0026] Next, as shown in Fig. 1D, the porous SiO₂ film 106 is subjected to H (hydrogen) plasma treatment. Thus, a dangling bond in an Si-O bond on the inner surface of the voids is replaced by an Si-H bond. As a result, the film improves in moisture absorption resistance.

[0027] Subsequently, as shown in Fig. 1E, an SiO_2 film 107 is formed on the porous SiO_2 film 106 subjected to the H (hydrogen) plasma treatment. This SiO_2 film 107 is formed by the plasma enhanced CVD method. SiH_4 and N_2O are used as the reaction gas.

[0028] Next, as shown in Fig. 1F, an SiO_2 film 108 is formed on the SiO_2 film 107. This SiO_2 film 108 is formed in order to planarize the surface. The SiO_2 film 108 is formed by the CVD method using TEOS (Tetra-Ethyl-Ortho-Silicate) and O3 as the reaction gas. A density of O_3 for use in this case is the density enough to oxidize TEOS. Thus, the SiO_2 film 108 is a fluidic SiO_2 film. The thickness of the SiO_2 film 108 is 200 nm.

[0029] Subsequently, as shown in Fig. 1G, the surface of the SiO₂ film 108 is planarized by etching or CMP method (Chemical Mechanical Polishing method). At this time, the respective SiO₂ films 105, 106 and 107 previously formed are partly removed by the etching. The planarizing by the etching is such that the SiO₂ film 105 formed on a convexity 103a of the aluminum wiring layer is not completely removed.

[0030] Subsequently, as shown in Fig. 1H, an SiO_2 film 109 (a cover insulating film) is formed on the planarized surface. This SiO_2 film 109 is formed by the plasma enhanced CVD method. SiH_4 and N_2O are used as the reaction gas. The thickness of the SiO_2 film 109 is 100 nm.

[0031] The interlayer insulating film having good heat proof and moisture absorption resistance and a low dielectric constant is formed on the substrate 104 by the SiO_2 films 105 (the underlying insulating film), 106, 107 and 109 (the cover insulating film) which are formed as described above. That is, the SiO_2 film 106 is porous and thus the dielectric constant of the SiO_2 film 106 is 2.0 to 3.0. These values are lower than the dielectric constant 4.0 of a typical SiO_2 film. Moreover, the typical SiO_2 film 109 is formed on the porous SiO_2 film 106. Thus, it is possible to prevent moisture from penetrating into the SiO_2 film 106. Furthermore, the heat proof of the SiO_2 films 105, 106, 107 and 109 is better than that of an organic insulating film.

[0032] In the above-described example, Si_2H_6 and O_3 are used as the reaction gas in order to toxin the porous SiO_2 film 106. However, other reaction gases can be used to form the similar porous SiO_2 film to the above-exemplified porous SiO_2 film. Such reaction gases are as follows:

 $Si_2H_6 + O_2$, $Si_3H_8 + O_3$, or $Si_3H_8 + O_2$.

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[0033] Furthermore, a B-containing reaction gas and an F-containing reaction gas are used in addition to the above-mentioned reaction gases, whereby a porous B-containing SiO₂ film and a porous F-containing SiO₂ film can be formed

(b) Second embodiment

45 [0034] The second embodiment is obtained by applying the first embodiment to a damascene process.

[0035] Figs. 2A to 2M are cross sectional views for describing the second embodiment.

[0036] First, as shown in Fig. 2A, a BPSG (borophosphosilicate glass) film 202 is formed on a silicon substrate 201. An aluminum layer is formed on the BPSG film 202 and then the aluminum layer is patterned, whereby an aluminum wiring layer 203 is formed. A substrate 204 comprises the silicon substrate 201, the BPSG film 202 and the aluminum wiring layer 203.

[0037] Subsequently, as shown in Fig. 2B, an SiO_2 film 205 (the underlying insulating film) having a thickness of 100 nm is formed on the aluminum wiring layer 203. This SiO_2 film 205 is formed by the plasma enhanced CVD method. SiH_4 and N_2O are used as the reaction gas.

[0038] Then, as shown in Fig. 2C, an SiO_2 film 206 is formed on the SiO_2 film 205 (the underlying insulating film). This SiO_2 film 206 is formed by the CVD method using Si_2H_6 and O_3 as the reaction gas. When these reaction gases are used, particulate SiO_2 is formed in the vapor phase and the particulate SiO_2 is deposited on the SiO_2 film 205. Thus, the SiO_2 film 206 has many voids in the film. Consequently, the SiO_2 film 206 is a porous SiO_2 film. The thickness of the porous SiO_2 film 206 is 500 nm.

[0039] Next, as shown in Fig. 2D, the porous SiO₂ film 206 is subjected to the H (hydrogen) plasma treatment. Thus, the dangling bond in the Si-O bond on the inner surface of the voids is replaced by the Si-H bond. Therefore, the film improves in the moisture absorption resistance.

[0040] Next, as shown in Fig. 2E, an SiO_2 film 207 is formed on the porous SiO_2 film 206. This SiO_2 film 207 is formed by the plasma enhanced CVD. SiH_4 and N_2O are used as the reaction gas. The SiO_2 film 207 can prevent Cu of a Cu-plated film to be later formed on the SiO_2 film 207 from diffusing into the porous SiO_2 film 206.

[0041] Subsequently, as shown in Fig. 2F, the SiO₂ films 205 (the underlying insulating film), 206 and 207 are opened by patterning, whereby a damascene trench 208 is formed. This damascene trench 208 communicates with the aluminum wiring layer 203 formed under the SiO₂ film 205.

[0042] Next, as shown in Fig. 2G, an SiO_2 film 209 (a first insulating film) is formed on the SiO_2 film 207 and on sides and a bottom of the damascene trench 208. This SiO_2 film 209 is formed by the plasma enhanced CVD method. The SiO_2 film 209 formed on the sides of the damascene trench 208 can prevent Cu to be later buried in the damascene trench 208 from diffusing into the porous SiO_2 film 206.

[0043] Next, as shown in Fig. 2H, the SiO_2 film 209 (the first insulating film) is anisotropically etched. Thus, the SiO_2 film 209 is removed leaving a portion of the SiO_2 film 209 formed on the sides of the damescene trench 208. Consequently, a contact hole communicating with the aluminum wiring layer 203 is formed in the bottom of the damascene trench 208. The SiO_2 film 207 remains on the porous SiO_2 film 206 without being removed by this etching.

[0044] Subsequently, as shown in Fig. 2I, a Cu-plated film 210 is formed in the damascene trench 208 and on the SiO_2 film 207. The Cu-plated film 210 formed in the damascene trench 208 is used as Cu wiring layer.

[0045] Next, as shown in Fig. 2J, the Cu-plated film 210 formed on the SiO_2 film 207 is polished and removed by the CMP method. Thus, the Cu-plated film remains only in the damascene trench 208.

[0046] Subsequently, as shown in Fig. 2K, a TiN film 211 for a barrier metal is formed on the damascene trench 208. This TiN film 211 can prevent Cu in the damascene trench 208 from diffusing into the SiO₂ film to be later formed on the damascene trench 208.

[0047] Next, as shown in Fig. 2L, the patterning leaves a TiN film 211a formed on the damascene trench 208 and etches away the TiN film 211 formed on the other portion.

[0048] Subsequently, as shown in Fig. 2M, an SiO_2 film 212 (the cover insulating film) is formed on the SiO_2 film 207 and the TiN film 211a. This SiO_2 film 212 is formed by the plasma enhanced CVD method. SiH_4 and N_2O are used as the reaction gas.

[0049] As described above, the interlayer insulating film having the good heat resistivity and moisture absorption resistance and the low dielectric constant is formed on the substrate 204. That is, the SiO₂ film 206 is porous and thus the dielectric constant of the SiO₂ film 206 is 2.0 to 3.0. These values are lower than the dielectric constant 4.0 of a typical nonporous SiO₂ film. Moreover, the typical SiO₂ films 207 and 212 (the cover insulating film) are formed on the porous SiO₂ film 206. Thus, it is possible to prevent the moisture from penetrating into the porous SiO₂ film 206. Furthermore, the heat resistivity of the SiO₂ films 206, 207 and 212 is better than that of the organic insulating film.

[0050] In the above-described example, Si_2H_6 and O_3 are used as the reaction gas in order to form the porous SiO_2 film 206. However, other reaction gases can be used to form the similar porous SiO_2 film to the above-exemplified porous SiO_2 film. Such reaction gases are as follows:

 $Si_2H_6 + O_2$, $Si_3H_8 + O_3$, or

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Si₃H₈ + O₂.

[0051] Furthermore, the B-containing reaction gas and the F-containing reaction gas are used in addition to the above-mentioned reaction gases, whereby the porous B-containing SiO₂ film and the porous F-containing SiO₂ film can be formed.

(c) Third embodiment

[0052] Figs. 3A to 3I are cross- sectional views for describing the third embodiment. Fig. 4 is a graph showing time dependency of an SiH₄ flow rate, an O₂ flow rate, an Ar flow rate and an RF power applied to a chamber in the third embodiment.

[0053] First, as shown in Fig. 3A, a BPSG (borophosphosilicate glass) film 302 is formed on a silicon substrate 301. The aluminum layer is formed on the BPSG film 302 and then the aluminum layer is patterned, whereby an aluminum wiring layer 303 is formed. A substrate 304 comprises the silicon substrate 301, the BPSG film 302 and the aluminum wiring layer 303.

[0054] Then, as shown in Fig. 3B, an SiO_2 film 305 (the underlying insulating film) of 100 nm in thickness is formed on the aluminum wiring layer 303. This SiO_2 film 305 is formed by low pressure CVD method using SiH_4 and O_2 as the

reaction gas under a pressure of 1 Torr with the silicon substrate 301 kept at 400°C.

[0055] Subsequently, as shown in Fig. 3C, a porous SiO_2 film 306 is formed on the SiO_2 film 305 (the underlying insulating film). This SiO_2 film 306 is formed by applying the RF power shown in Fig. 4 to the chamber using SiH_4 and O_2 as the reaction gas with the silicon substrate 301 kept at 400 °C As can be seen from Fig. 4, during film formation, the SiH_4 flow rate and the O_2 flow rate are fixed, whereas the RF power is applied to the chamber at a cycle of 10 sec. Thus, plasma is generated and disappears at every cycle of 10 sec. While the plasma is generated, Ar is introduced into the chamber in order to control the pressure in the chamber. The use of the plasma changing with time allows the process using the low pressure CVD and the process using the plasma enhanced CVD under a low pressure to repeat in one chamber. For example, in Fig. 4, the plasma is not generated during a time period from 0 sec to 5 sec, and thus the process using the low pressure CVD is performed. The plasma is generated during the time period from 5 sec to 10 sec, and thus the process using the plasma enhanced CVD under the low pressure is lower than the pressure (2.0 Torr) in the chamber during the plasma enhanced CVD under the low pressure. Moreover, the RF power with a frequency of 13.56 MHz and the RF power with a frequency of 400 kHz are used in order to generate the plasma. The low pressure CVD and the plasma enhanced CVD under the low pressure are repeated in this manner, whereby the SiO_2 film having many voids is formed. That is, the SiO_2 film 306 is porous.

[0056] Next, as shown in Fig. 3D, the porous SiO₂ film 306 is subjected to the H (hydrogen) plasma treatment. Thus, the dangling bond in the Si-O bond on the inner surface of the voids is replaced by the Si-H bond. Accordingly, the film improves in the moisture absorption resistance.

[0057] Then, as shown in Fig. 3E, an SiO_2 film 307 is formed on the porous SiO_2 film 306 subjected to the H (hydrogen) plasma treatment. This SiO_2 film 307 is formed by the low pressure CVD method. SiH_4 and O_2 are used as the reaction gas.

[0058] Next, as shown in Fig. 3F, an SiO_2 film 308 is formed on the SiO_2 film 307. This SiO_2 film 308 is formed in order to planarize the surface. The SiO_2 film 308 is formed by the CVD method using TEOS (Tetra-Ethyl-Ortho-Silicate) and O_3 as the reaction gas. The density of O_3 for use in this case is enough to oxidize TEOS. Thus, the SiO_2 film 308 is a fluidic SiO_2 film.

[0059] Subsequently, as shown in Fig. 3G, the surface of the SiO₂ film 308 is polished and planarized by the CMP method (Chemical Mechanical Polishing method). At this time, the respective SiO₂ films 305, 306 and 307 previously formed are partly polished and removed. The planarizing by the CMP method is such that the SiO₂ film 305 formed on a convexity 303a of the aluminum wiring layer is not completely removed.

[0060] Next, as shown in Fig. 3H, a porous SiO_2 film 309 is formed on the planarized surface. This SiO_2 film 309 is formed by repeating the low pressure CVD and the plasma enhanced CVD similarly to the porous SiO_2 film 306 previously formed. That is, the SiO_2 film 309 is formed by using pulse plasma shown in Fig. 10 in an atmosphere of Ar using SiH_4 and O_2 as the reaction gas with the silicon substrate 301 kept at 400 °C. The pressure in the chamber during the low pressure CVD is 1 Torr. This pressure is lower than the pressure (2.0 Torr) in the chamber during the plasma enhanced CVD under the low pressure.

[0061] Then, as shown in Fig. 3I, the porous SiO_2 film 309 is subjected to the H (hydrogen) plasma treatment. Thus, the dangling bond in the Si-O bond on the inner surface of the voids is replaced by the Si-H bond. Therefore, the film improves in the moisture absorption resistance.

[0062] The interlayer insulating film having the good heat resistivity and moisture absorption resistance and the low dielectric constant is formed on the substrate 304 with the SiO_2 films 305 (the underlying insulating film), 306, 307 and 309 which are formed as described above. That is, the SiO_2 films 306 and 309 are porous and thus the dielectric constant of the SiO_2 films 306 and 309 is 2.0 to 3.0. These values are lower than the dielectric constant 4.0 of the typical nonporous SiO_2 film. Moreover, the porous SiO_2 films 306 and 309 are subjected to the H (hydrogen) plasma treatment, whereby the film improves in the moisture absorption resistance. Additionally, the heat resistivity of the SiO_2 films 305, 306, 307 and 309 is better than that of the organic insulating film.

[0063] In the aforementioned example, SiH_4 and O_2 are used as the reaction gas for forming the porous SiO_2 films 306 and 309. However, other reaction gases can be used to form the similar film. Such reaction gases are as follows:

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50 SiH compound + O_2,
SiH compound + O_3 + O_2,
Si-C-O-H compound + O_2, or
Si-C-O-H compound + O_3 + O_2.
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[0064] In the above compounds such as the SiH compound and Si-C-O-H compound, a general formula Si_nH_{2n+2} (n = 1 to 2) may be used as the SiH compound. A general formula $Si(OR)_nH_{4-n}$ (R = C_mH_{2m+1} (m = 1, 2), n = 1 to 4) may be used as the Si-C-O-H compound.

[0065] Those are the same in the following embodiment.

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(d) Fourth embodiment

[0066] The fourth embodiment is obtained by applying the third embodiment to the damascene process.

[0067] Figs. 5A to 5M are cross- sectional, views for describing the fourth embodiment. Fig. 4 is the graph showing the time dependency of the SiH₄ flow rate, the O₂ flow rate, the Ar flow rate and the RF power applied to the chamber in the fourth embodiment.

[0068] First, as shown in Fig. 5A, a BPSG (borophosphosilicate glass) film 402 is formed on a silicon substrate 401. An aluminum layer is formed on the BPSG film 402 and then the aluminum layer is patterned, whereby an aluminum wiring layer 403 is formed. A substrate 404 comprises the silicon substrate 401, the BPSG film 402 and the aluminum wiring layer 403.

[0069] Then, as shown in Fig. 5B, an SiO_2 film 405 (the underlying insulating film) of 100 nm thick is formed on the aluminum wiring layer 403. This SiO_2 film 405 is formed by the low pressure CVD method using SiH_4 and O_2 as the reaction gas under a pressure of 1 Torr with the silicon substrate 401 kept at 400 °C.

[0070] Subsequently, as shown in Fig. 5C, a porous SiO_2 film 406 is formed on the SiO_2 film 405 (the underlying insulating film). This SiO_2 film 406 is formed by applying the RF power shown in Fig. 4 to the chamber using SiH_4 and O_2 as the reaction gas with the silicon substrate 401 kept at 400 °C. As can be seen from Fig. 4, during the film formation, the SiH_4 flow rate and the O_2 flow rate are fixed, whereas the RF power is applied to the chamber at a cycle of 10 sec. Thus, the plasma is generated and disappears at every cycle of 10 sec. While the plasma is generated, Ar is introduced into the chamber in order to control the pressure in the chamber. The use of the plasma changing with the time permits the process using the low pressure CVD and the process using the plasma enhanced CVD under the low pressure to repeat in one chamber. For instance, in Fig. 4, the plasma is not generated during the time period from 0 sec to 5 sec, and thus the process using the low pressure CVD is performed. The plasma is generated during the time period from 5 sec to 10 sec, and thus the process using the plasma enhanced CVD under the low pressure is lower than the pressure in the chamber during the plasma enhanced CVD under the low pressure. Moreover, the RF power with a frequency of 13.56 MHz and the RF power with a frequency of 400 kHz are used in order to generate the plasma. The low pressure CVD and the plasma enhanced CVD under the low pressure are repeated in this way, whereby the SiO_2 film having many voids is formed. That is, the SiO_2 film 406 is porous. The SiO_2 film 406 has a thickness of 300 nm.

[0071] Then, as shown in Fig. 5D, the porous SiO_2 film 406 is subjected to the H (hydrogen) plasma treatment. Thus, the dangling bond in the Si-O bond on the inner surface of the voids is replaced by the Si-H bond. Therefore, the film improves in the moisture absorption resistance.

[0072] Subsequently, as shown in Fig. 5E, the SiO_2 films 405 (the underlying insulating film) and 406 are opened by patterning, whereby a damascene trench 407 is formed. This damascene trench 407 communicates with to the aluminum wiring layer 403 formed under the SiO_2 film 405.

[0073] Next, as shown in Fig. 5F, an SiO₂ film 408 (the first insulating film) is formed on the SiO₂ film 406 and on the sides and the bottom of the damascene trench 407. This SiO₂ film 408 is formed by the plasma enhanced CVD method. The SiO₂ film 408 formed on the sides of the damascene trench 407 can prevent Cu to be later buried in the damascene trench 407 from diffusing into the porous SiO₂ film 406. The SiO₂ film 408 has a thickness of 100 nm.

[0074] Next, as shown in Fig. 5G, the SiO₂ film 408 (the first insulating film) is anisotropically etched. Thus, the SiO₂ film 408 is removed leaving a portion of the SiO₂ film 408 formed on the sides of the damascene trench 407. Consequently, the contact hole communicating with the aluminum wiring layer 403 is formed in the bottom of the damascene trench 407.

[0075] Subsequently, as shown in Fig. 5H, a Cu-plated film 409 is formed in the damascene trench 407 and on the SiO_2 film 406. The Cu-plated film 409 formed in the damascene trench 407 is used as the Cu wiring layer.

[0076] Next, as shown in Fig. 5I, the Cu-plated film 409 formed on the SiO₂ film 406 is polished and removed by the CMP method. Thus, the Cu-plated film remains only in the damascene trench 407.

[0077] Then, as shown in Fig. 5J, a TiN film 410 for the barrier metal is formed on the damascene trench 407. This TiN film 410 can prevent Cu in the damascene trench 407 from diffusing into the SiO₂ film to be later formed on the damascene trench 407.

50 [0078] Then, as shown in Fig. 5K, the patterning leaves a TiN film 410a formed on the damascene trench 407 and etches away the TiN film 410 formed on the other portion.

[0079] Then, as shown in Fig. 5L, a porous SiO_2 film 411 is formed on the SiO_2 film 406 and the TiN film 410a. This SiO_2 film 411 is formed by repeating the low pressure CVD and the plasma enhanced CVD similarly to the porous SiO_2 film 406 previously formed. That is, the SiO_2 film 411 is formed by applying the pulse plasma (the plasma which is periodically generated and disappears) shown in Fig. 4 in the atmosphere of Ar using SiH_4 and O_2 as the reaction gas with the silicon substrate 401 kept at 400 °C. In this case, the RF power applied to generate the plasma has a frequency of 13.56 MHz. The pressure in the chamber during the low pressure CVD is 1 Torr. This pressure is lower than the pressure in the chamber during the plasma enhanced CVD under the low pressure. The SiO_2 film 411 has a thickness of

500 nm.

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[0080] Then, as shown in Fig. 5M, the porous SiO₂ film 411 is subjected to the H (hydrogen) plasma treatment. Thus, the dangling bond in the Si-O bond on the inner surface of the voids is substituted with the Si-H bond. Therefore, the film improves in the moisture absorption resistance.

[0081] As described above, the interlayer insulating film having the good heat resistivity and moisture absorption resistance and the low dielectric constant is formed on the substrate 404. That is, the SiO₂ films 406 and 411 are porous and thus the dielectric constant of these films is 2.0 to 3.0. These values are lower than the dielectric constant 4.0 of the typical nonporous SiO₂ film. Moreover, the porous SiO₂ films 406 and 411 undergo the H (hydrogen) plasma treatment, whereby the film improves in the moisture absorption resistance. Furthermore, the heat resistivity of the SiO₂ films 406 and 411 is better than that of the organic insulating film.

[0082] In the above-described example, SiH_4 and O_2 are used as the reaction gas for forming the porous SiO_2 films 406 and 411. However, other reaction gases can be used to form the similar film. Such reaction gases are as follows:

SiH compound + O_2 , SiH compound + O_3 , Si-C-O-H compound + O_2 , or Si-C-O-H compound + O_3 .

(e) Fifth embodiment

[0083] Figs. 6A to 6J are cross sectional views for describing the fifth embodiment. Fig. 7 is a graph showing the time dependency of the flow rate of the reaction gas (a CH compound) for forming an organic film, the flow rate of the reaction gas (SiH₄) for forming the SiO_2 film, the O_2 flow rate and the gas (Ar) for controlling the pressure in the fifth embodiment.

[0084] First, as shown in Fig. 6A, a BPSG (borophosphosilicate glass) film 502 is formed on a silicon substrate 501. An aluminum film is formed on the BPSG film 502 and then the aluminum film is patterned, whereby an aluminum wiring layer 503 is formed. A substrate 504 comprises the silicon substrate 501, the BPSG film 502 and the aluminum wiring layer 503 which are formed in this manner.

[0085] Then, as shown in Fig. 6B, an SiO_2 film 505 (the underlying insulating film) of 100 nm thick is formed on the aluminum wiring layer 503. This SiO_2 film 505 is formed, by the low pressure CVD method using SiH_4 and O_2 as the reaction gas under a pressure of 1 Torr with the silicon substrate 501 kept at 400 °C.

[0086] Then, as shown in Fig. 6C, a film 506 is formed on the SiO_2 film 505 by depositing the organic film and the SiO_2 film alternately. The film 506 having the organic film alternating with the SiO_2 film is formed by alternately introducing the reaction gas for forming the organic film and the reaction gas for forming the SiO_2 film into the chamber which the RF power with a frequency of 13.56 MHz and the RF power with a frequency of 400 kHz are applied to. The SiO_2 film is formed on the uppermost layer of the film 506. For example, in Fig. 7, the SiO_2 film is formed during the tine period from 0 sec to 5 sec, and the organic film is formed during the time period from 5 sec to 10 sec. In this embodiment, TEOS (Tetra-Ethyl-Ortho-Silicate) or $Si(CH_3)H_3$ is used as the reaction gas for forming the organic film, and SiH_4 is used as the reaction gas for forming the SiO_2 film.

[0087] Then, as shown in Fig. 6D, the film 506 having the organic film alternating with the SiO_2 film is subjected to ashing by O (oxygen) plasma. Thus, the organic film is ashed, so that the voids are created in an area in which the organic film was formed. Consequently, the film 506 having the organic film alternating with the SiO_2 film is changed to a porous SiO_2 film 507.

[0088] Subsequently, as shown in Fig. 6E, the porous SiO₂ film 507 is subjected to the H (hydrogen) plasma treatment. Thus, the dangling bond in the Si-O bond on the inner surface of the voids is substituted with the Si-H bond. Therefore, the film improves in the moisture absorption resistance.

[0089] Then, as shown in Fig. 6F, an SiO_2 film 508 is formed on the porous SiO_2 film 507 subjected to the H (hydrogen) plasma treatment. This SiO_2 film 508 is formed by the low pressure CVD method. SiH_4 and O_2 are used as the reaction gas.

[0090] Then, as shown in Fig. 6G, an SiO_2 film 509 is formed on the SiO_2 film 508. This SiO_2 film 509 is formed in order to planarize the surface. The SiO_2 film 509 is formed by the CVD method using TEOS (Tetra-Ethyl-Ortho-Silicate) and O_3 as the reaction gas. The density of O_3 for use in this case is sufficient to oxidize TEOS. Thus, the SiO_2 film 509 is a fluidic SiO_2 film.

[0091] Subsequently, as shown in Fig. 6H, the surface of the SiO₂ film 509 is polished and planarized by the CMP method. At this time, the SiO₂ film (the underlying insulating film) 505, the porous SiO₂ film 507 and the SiO₂ film 508 previously formed are partly polished and removed. The planarizing by the CMP is such that the SiO₂ film 505 formed on a convexity 503a of the aluminum wiring layer is not completely removed.

[0092] Then, as shown in Fig. 6I, a porous SiO₂ film 510 is formed on the planarized surface. This SiO₂ film 510 is

formed in the same manner as the porous SiO_2 film 507 previously formed. That is, the organic film and the SiO_2 film are alternately deposited by alternately introducing the reaction gas for forming the organic film and the reaction gas for forming the SiO_2 film into the chamber which the RF power with a frequency of 13.56 MHz and the RF power with a frequency of 400 kHz are applied to. Then, the obtained film is subjected to ashing by the O (oxygen) plasma. Thus, the organic film is ashed, so that the voids are created in the area in which the organic film was formed. As a result, the porous SiO_2 film 510 was formed. In this embodiment, the CH containing compound is used as the reaction gas for forming the organic film, and SiH_4 and O_2 are used as the reaction gas for forming the SiO_2 film.

[0093] Subsequently, as shown in Fig. 6J, the porous SiO₂ film 510 is subjected to the H (hydrogen) plasma treatment. Thus, the dangling bond in the Si-O bond on the inner surface of the voids is substituted with the Si-H bond. Consequently, the film improves in the moisture absorption resistance.

[0094] The interlayer insulating film having the good heat resistivity and moisture absorption resistance and the low diel ectric constant is formed on the substrate 504 with the SiO_2 films 505 (the underlying insulating film), 507, 508 and 510 which are formed as described above. That is, the SiO_2 films 507 and 510 are porous and thus the dielectric constant of these films is 2.0 to 3.0. These values are lower than the dielectric constant 4.0 of the typical nonporous SiO_2 film. Moreover, the porous SiO_2 films 507 and 510 undergo the H (hydrogen) plasma treatment, whereby the film improves in the moisture absorption resistance. Furthermore, the heat resistivity of the SiO_2 films 505, 507, 508 and 510 is better than that of the organic insulating film.

[0095] In the above-described example, the CH containing compound, SiH_4 and O_2 are used as the reaction gas which is alternately introduced into the chamber in order to form the porous SiO_2 films 507 and 510. However, the reaction gas for forming the porous SiO_2 film is not limited to these reaction gases. For example, a CF containing compound is used instead of SiH_4 of the above -mentioned reaction gases, whereby the porous F-containing SiO_2 film can be formed.

[0096] In the above compounds such as the CH compound and CF compound, a general formula C_nH_{2n+2} (n = 1 to 3) may be used as the CH compound. A general formula $F_nSi(OR)_{4-n}$ (R = C_mH_{2m+1} (m = 1, 2), n = 1 to 4) of which $Fsi(OC_2H_5)_3$ is typical, or some compounds containing carbon and fluorine may be used as the CF compound.

[0097] Those are the same in the following embodiment.

[0098] Besides, in the above third to fifth embodiments, the cover insulating film 109 as shown in FIG. 1H may be formed in place of the porous insulating film 309, 411, 510.

[0099] Further, in the above first and second embodiments, the porous insulating film 309, 411, 510 in the above third to fifth embodiments may be formed in place of the cover insulating film 109.

(2) Description of a semiconductor manufacturing apparatus according to a sixth embodiment of the present invention

[0100] The semiconductor manufacturing apparatus according to the sixth embodiment will be described with reference to Figs. 4, 7 and 8.

[0101] Fig. 8 shows a constitution of the semiconductor manufacturing apparatus according to the sixth embodiment. In this drawing, numeral 613 denotes the chamber for forming the film. Numeral 611 denotes a gas inlet for introducing the reaction gas into the chamber 613. Numeral 615 denotes a wafer. Numeral 612 denotes a gas emitter for uniformly dispersing the reaction gas onto the wafer 615. Numeral 614 denotes a wafer holder containing a heater. Numeral 616 denotes a gas outlet for exhausting the reaction gas out of the chamber 613.

[0102] Numeral 610 denotes a pipe connected to the gas inlet 611. Branch pipes 606, 607, 608 and 609 are connected to an upstream of the pipe 610. The branch pipe 606 is used to supply Ar (argon). The branch pipe 607 is used to supply the CH containing compound. The branch pipe 608 is used to supply O_2 . The branch pipe 609 is used to supply O_3 . Furthermore, MFCs (means for controlling the flow rate) are disposed between these branch pipes. Control signals 619, 620, 621 and 622 are inputted from control means 601 to the MFCs. The reaction gas is controlled by these control signals so that the reaction gas is supplied at a desired flow rate.

[0103] Numeral 618 denotes a high-frequency power generator for applying the RF power with a frequency of 13.56 MHz between the gas emitter 612 and the chamber 613. Numeral 617 denotes switching means for supplying the RF power generated by the high-frequency power generator 618 to the chamber.

[0104] Numeral 624 denotes the high-frequency power generator for applying the RF power with a frequency of 400 kHz between the substrate stand 614 and the chamber 613. Numeral 625 denotes the switching means for supplying the RF power generated by the high-frequency power generator 624 to the chamber 613.

[0105] Control signals 623 and 626 are inputted from the control means 601 to the switching means 617 and 625, respectively, so that the time of application of the RF power is controlled.

[0106] Figs. 4 and 7 show the flow rate of the reaction gas and the time of application of the RF power which are controlled by the control means 601.

[0107] As shown in Fig. 4, during the film formation, MFC 602 (for supplying Ar), MFC 604 (for supplying O_2) and MFC 605 (for supplying SiH_4) keep open under the control signals 619, 621 and 622, and thus Ar, O_2 and SiH_4 are

always introduced into the chamber. Since the reaction gas is always exhausted through the gas outlet 616, the chamber 613 is kept at the low pressure. During the time period from 5 sec to 10 sec, the switching means 617 and 625 are turned on by the control signals 623 and 626, respectively, so that the RF power with a frequency of 13.56 MHz and the RF power with a frequency of 400 kHz are applied to the chamber 613. Thus, during the time period from 5 sec to 10 sec, the plasma enhanced CVD method under the low pressure is carried out in the atmosphere of Ar, O_2 and SiH₄.

[0108] On the other hand, in the drawing, during the time period from 10 sec to 15 sec, the switching means 617 and 625 are turned off and thus the RF power is not applied to the chamber 613. Thus, the low pressure CVD method is performed in the atmosphere of O_2 and SiH_4 . After 15 sec, the plasma enhanced CVD method under the low pressure and the low pressure CVD method are alternately repeated.

[0109] As described in the third and fourth embodiments, the plasma enhanced CVD method under the low pressure and the low pressure CVD method are thus repeated in the atmosphere of Ar, O₂ and SiH₄, whereby the porous SiO₂ film can be formed on the substrate.

[0110] Fig. 7 shows another example of the reaction gas flow rate which is controlled by the control means 601.

[0111] In this drawing, only the flow rate of the reaction gas is changed, and a level (not shown) of the RF power applied to the chamber is not changed. This is because the switching means 617 and 625 are always on under the control signals 623 and 626 during the film formation. The flow rates of O₂ and Ar change with time as shown in the drawing because the MFC 604 (for supplying O₂) and the MFC 602 (for supplying Ar) are controlled by the control signals 619 and 621.

[0112] During the time period from 5 sec to 10 sec in the drawing, MFC 603 (for supplying the CH containing compound) is opened by the control signal 620, so that the CH containing compound is introduced into the chamber 613 which the RF power is applied to. At the same time, the MFC 605 (for supplying SiH_4) is closed by the control signal 622. Thus, the atmosphere in the chamber is changed to the atmosphere of the CH containing compound and O_2 , and the organic film is formed on the wafer 615 by the plasma enhanced CVD method.

[0113] On the other hand, during the time period from 10 sec to 15 sec in the drawing, the MFC 603 (for supplying the CH containing compound) is closed by the control signal 620, so that the introduction of the CH containing compound into the chamber is stopped. At the same time, the MFC 605 (for supplying SiH_4) is opened by the control signal 622. Thus, SiH_4 is introduced into the chamber 613 which the RF power is applied to. Then, the SiO_2 film is formed on the wafer 615 by the plasma enhanced CVD method in the atmosphere of O_2 and SiH_4 . After 15 sec, the process for forming the organic film and the process for forming the SiO_2 film are alternately repeated, whereby the organic film and the SiO_2 film are alternately laminated on the wafer 615.

[0114] As described in the fifth embodiment, the film having the organic film alternating with the SiO_2 film is ashed by the O (oxygen) plasma so that the organic film is selectively removed, whereby the porous SiO_2 film can be formed on the substrate.

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1. A method for forming an interlayer insulating film comprising the step of:

forming a porous SiO_2 film (106, 206) on a substrate (104, 204) by chemical vapor deposition using a reaction gas containing an oxidative gas and one selected from the group consisting of Si_2H_6 and Si_3H_8 as a reaction gas.

- A method according to claim 1, wherein said reaction gas contains a compound containing one selected from the group consisting of F (fluorine) and B (boron).
- A method according to claim 1, wherein said oxidative gas is O₂ or O₃.
- 4. A method according to claim 1, wherein said porous SiO₂ film (106, 206) is formed, and then said porous SiO₂ film (106, 206) is subjected to H (hydrogen) plasma treatment.
- A method according to claim 1, wherein said porous SiO₂ film (106, 206) is formed, and then a cover insulating film (109, 207, 212) is formed on said porous SiO₂ film (106, 206).
- 6. A method according to claim 1, further comprising the steps of:

forming said porous SiO_2 film (206) on said substrate (204) and then forming a damascene trench (208) in said porous SiO_2 film (206) by patterning;

forming a side wall insulating film (209) on sides of said damascene trench (208);

embedding a metal film (210) in said damascene trench (208); and forming a barrier metal layer (211a) on said metal film (210).

- A method according to claim 1, wherein an underlying insulating film (105, 205) is formed on said substrate (104, 204) and then said porous SiO₂ film (106, 206) is formed on said underlying insulating film (105, 205).
 - 8. A semiconductor device comprising an interlayer insulating film (106, 206) formed by a method for forming an interlayer insulating film according to claim 1.
- 9. A method for forming an interlayer insulating film comprising the steps of:

introducing an oxidative gas and one selected from the group consisting of an SiH containing compound and an Si-C-O-H containing compound as a reaction gas;

intermittently or periodically generating plasma under a low pressure;

reacting said reaction gas to form a porous SiO_2 film (306, 406) on a substrate (304, 404) by plasma enhanced chemical vapor deposition.

- 10. A method according to claim 9, wherein said SiH containing compound is SiH4.
- 11. A method according to claim 9, wherein said oxidative gas is O₂ or O₃.
 - 12. A method according to claim 9, wherein the pressure of said reaction gas in a state in which said plasma is generated is higher than the pressure of said reaction gas in a state in which said plasma is not generated.
- 25 13. A method according to claim 9, wherein said porous SiO₂ film (306, 406) is formed, and then said porous SiO₂ film (306, 406) is subjected to H (hydrogen) plasma treatment.
 - 14. A method according to claim 9, wherein said porous SiO₂ film (306, 406) is formed, and then a cover insulating film is formed on said porous SiO₂ film (306, 406).
 - 15. A method according to claim 9, further comprising the steps of:

forming said porous SiO_2 film (406) on said substrate (404) and then forming a damascene trench (407) in said porous SiO_2 film (406) by patterning;

forming a side wall insulating film (408) on sides of said damascene trench (407);

embedding a metal film (409) in said damascene trench (407); and

forming a barrier metal layer (410a) on said metal film (409).

16. A method according to claim 15, wherein said side wall insulating film is formed by the steps of:

forming said damascene trench (407) and then forming a first insulating film (408) on said interlayer insulating film (406), on the sides of said damascene trench (407) and on a bottom of said damascene trench (407); and anisotropically etching said first insulating film (408) to such an extent that said first insulating film (408) formed on the sides of said damascene trench (407) remains and said first insulating film (408) formed on the bottom of said damascene trench (407) is removed.

- 17. A semiconductor device comprising an interlayer insulating film (406) formed by a method for forming an interlayer insulating film according to claim 9.
- 50 18. A method for forming an interlayer insulating film comprising the steps of:

alternately laminating an organic film and an SiO₂ film on a substrate (504) by a plasma enhanced chemical vapor deposition in which said substrate (504) is exposed alternately and repetitively to an atmosphere of a reaction gas containing a CH containing compound and an atmosphere of a reaction gas containing an SiH containing compound and O₂; and

forming a porous SiO₂ film (507) on said substrate (504) by selectively ashing and removing said organic film.

19. A method according to claim 18, wherein said ashing is performed with O (oxygen) plasma.

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- 20. A method according to claim 18, wherein said porous SiO₂ film (507) is formed, and then said porous SiO₂ film (507) is subjected to the H (hydrogen) plasma treatment.
- 21. A method according to claim 18, wherein an underlying insulating film (505) is formed on said substrate (504) before alternately laminating said organic film and said SiO₂ film on said substrate.
 - 22. A method for forming an interlayer insulating film comprising the steps of:

alternately laminating an organic film and an SiO₂ film containing F (fluorine) on a substrate by the plasma enhanced chemical vapor deposition in which said substrate is exposed alternately and repetitively to the atmosphere of the reaction gas containing the CH containing compound and the atmosphere of the reaction gas containing the SiH containing compound, a CF containing compound and O₂; and forming a porous SiO₂ film containing F (fluorine) on said substrate by selectively ashing and removing said organic film.

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- 23. A method according to claim 22, wherein said ashing is performed with O (oxygen) plasma.
- 24. A method according to claim 22, wherein said porous SiO₂ film is formed, and then said porous SiO₂ film is subjected to the H (hydrogen) plasma treatment.

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- 25. A method according to claim 22, wherein an underlying insulating film is formed on said substrate before alternately laminating said organic film and said SiO₂ film on said substrate.
- 26. A semiconductor device comprising an interlayer insulating film formed by a method for forming an interlayer insulating film according to claim 22.
 - 27. An apparatus for forming an interlayer insulating film comprising:

a chamber (613) for forming a film;

pipes (606, 607, 608, 609, 610) for supplying a reaction gas to said chamber (613);

flow rate control means (602, 603, 604, 605) attached to said pipes (606, 607, 608, 609), for controlling a flow rate of said reaction gas;

high-frequency power generating means (618, 624) for applying a high-frequency power to said chamber (613);

switching means (617, 625) for inputting or shutting off said high-frequency power applied to said chamber (613); and

control means (601) for controlling said flow rate control means (602, 603, 604, 605) and said switching means (617, 625).

- 28. An apparatus according to claim 27, wherein said control means (601) controls said flow rate control means (602, 603, 604, 605), thereby intermittently or periodically changing the flow rate of said reaction gas.
 - 29. An apparatus according to claim 27, wherein said control means (601) controls said switching means (617, 625), thereby intermittently or periodically changing said high-frequency power applied to said chamber (613).

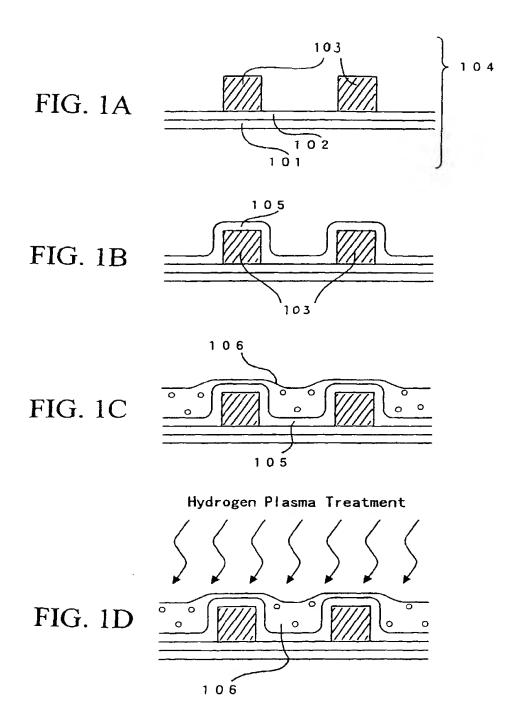
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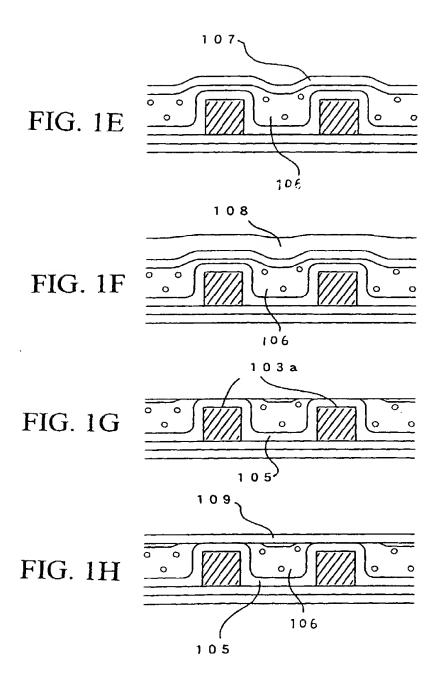
 An apparatus according to claim 29, wherein said reaction gas is an oxidative gas and an SiH containing compound.

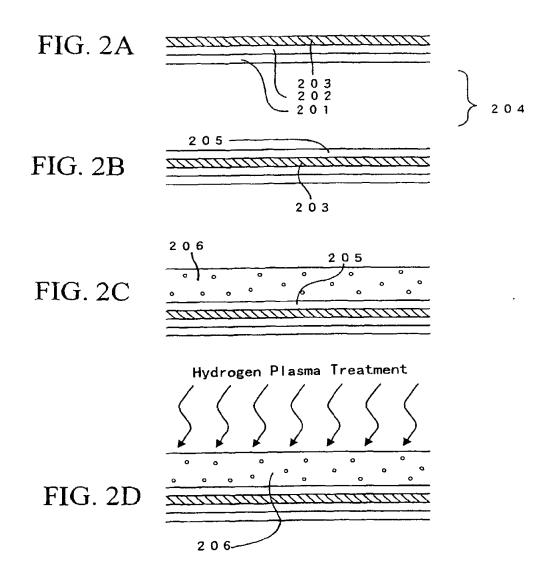
31. An apparatus according to claim 30, wherein said SiH containing compound is SiH₄.

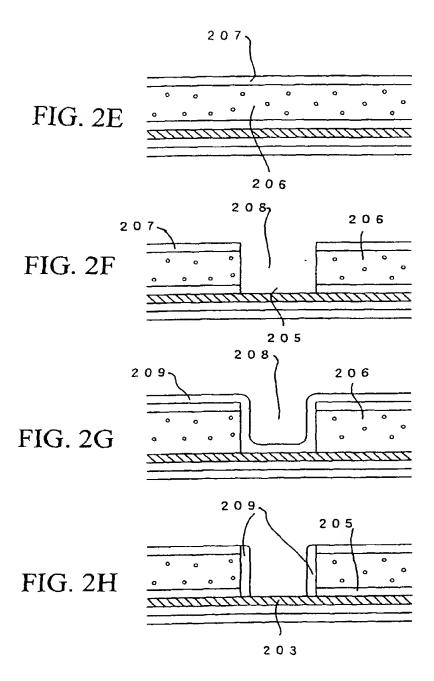
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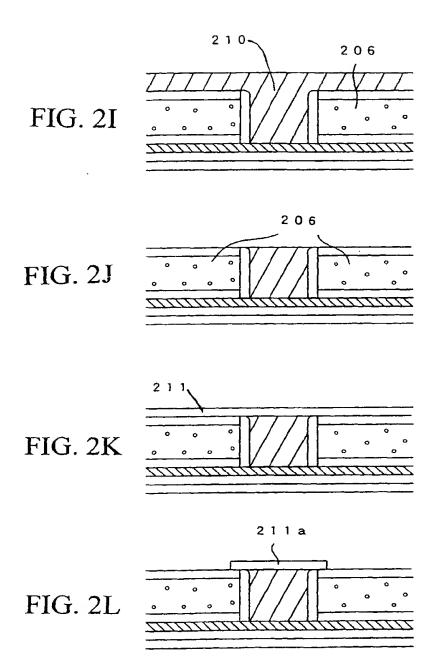
- 32. An apparatus according to claim 29, wherein said reaction gas is an oxidative gas and one selected from the group consisting of an Si-C-O-H containing compound and a CH containing compound.
- 33. An apparatus according to claim 32, wherein said oxidative gas is O2 or O3.

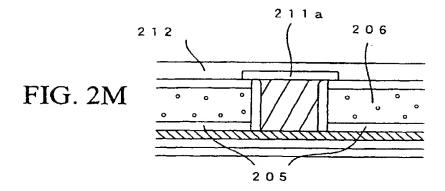


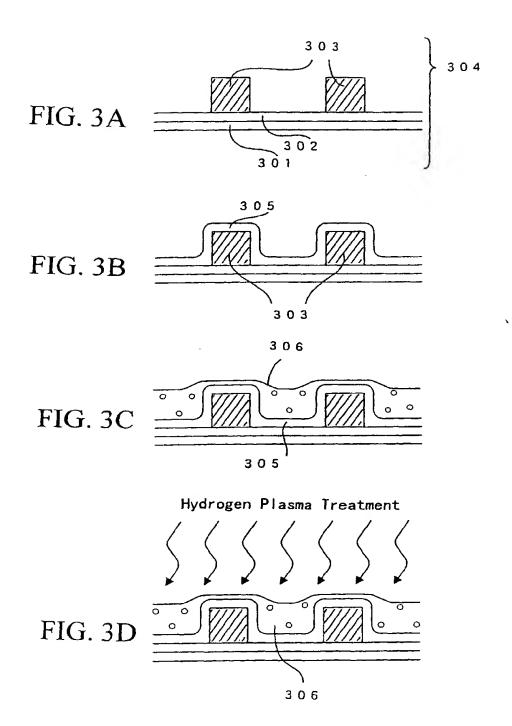


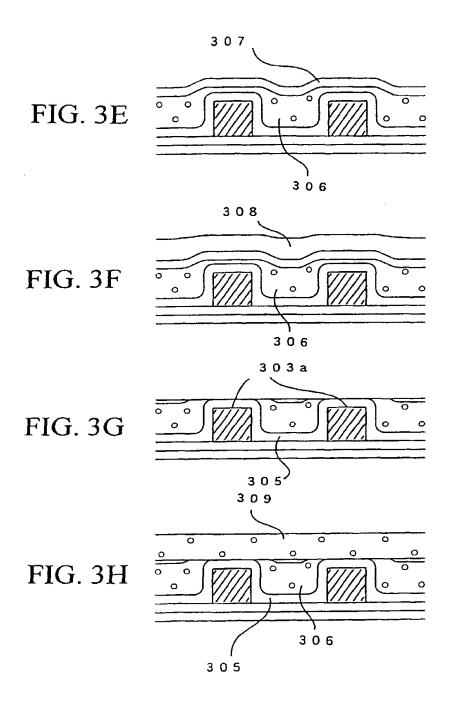


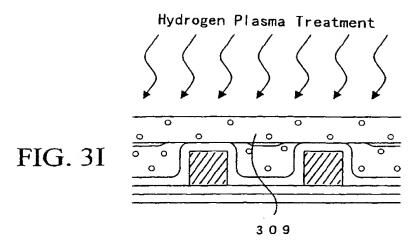


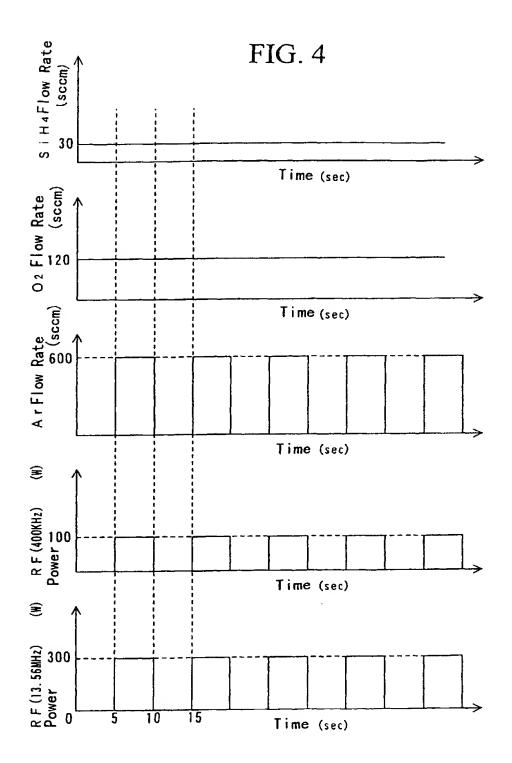


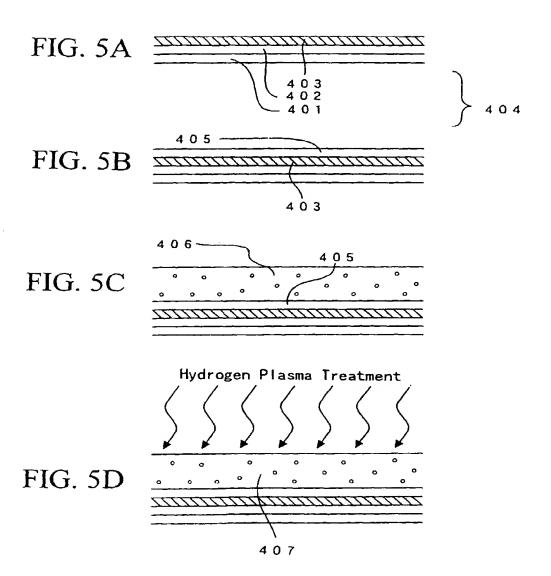


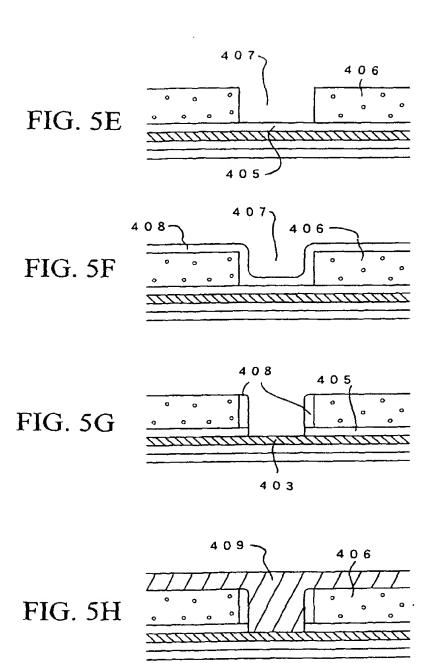












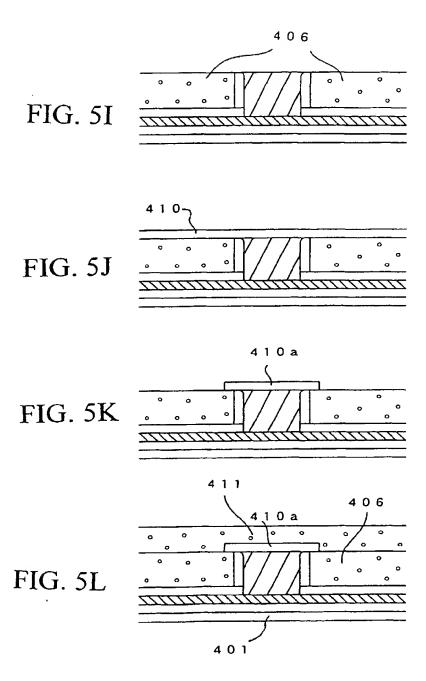


FIG. 5M

Hydrogen Plasma Treatment

